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JP 2000-12020

Omi, et al.

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to Seki, then the nonaqueous electrolyte rechargeable battery which both contains this electrolytic solution at the nonaqueous electrolyte for rechargeable batteries which it is still more detailed, and fire retardancy is high, was safe, and could generate the high voltage, and was excellent in the cell charge-and-discharge property about the nonaqueous electrolyte for rechargeable batteries, and a nonaqueous electrolyte rechargeable battery.

[0002]

[Background of the Invention] Nonaqueous electrolyte is used as the electrolytic solution of energy storage devices, such as a lithium cell, and since these devices have a high voltage and high energy density and are excellent in reliability, they are widely used for the power supply of consumer electronics etc. Nonaqueous electrolyte consists of a non-aqueous solvent and an electrolyte, and propylene carbonate [which is generally the organic solvent of a high dielectric constant], gamma-butyrolactone, sulfolane or dimethyl carbonate [that is the organic solvent of hypoviscosity], dimethoxyethane, tetrahydrofuran, 1, and 3-dioxolane etc. is used as a non-aqueous solvent. Moreover, as an electrolyte, Et₄NBF₄, LiBF₄, LiPF₆, LiClO₄ and LiAsF₆, LiCF₃SO₃, LiAlCl₄, LiSiF₆, etc. are used.

[0003] By the way, since a cell with high energy density is desired, research is advanced about the high-voltage cell. For example, the rechargeable battery called the rocking-chair mold which used the lithium of LiCoO₂, LiNiO₂, and LiMn₂O₄ grade and the multiple oxide of transition metals for the positive electrode of a cell, and used the carbon material for the negative electrode is studied. since [in this case,] cell voltage can generate more than 4V and moreover does not have a deposit of a metal lithium - a surcharge and external short-circuit -- ****(ing) -- crushing -- etc. -- also by experiment, it is checked that safety is secured and it appears on the market as a noncommercial use. However, when the future large formation of high energy density and enlargement are made, to raise safety further is desired and it is called for that inflammable nonaqueous electrolyte has self-extinguishing. For this reason, adding the phosphoric ester known as a compound with self-extinguishing to the electrolytic solution is proposed (for example, refer to JP,4-184870,A).

[0004] However, although the electrolytic solution which added general phosphoric ester, such as phosphoric-acid triethyl, is fire retardancy and safety improved, there were some which cannot necessarily be satisfied in respect of cell charge-and-discharge effectiveness, the energy density of a cell, and a battery life depending on the class or addition of phosphoric ester. Although limiting the addition of phosphoric ester (for example, referring to JP,7-114940,A) etc. was proposed in order to solve such a problem for example, it was not what is not necessarily satisfied in respect of fire retardancy, safety, cell charge-and-discharge effectiveness, the energy density of a cell, a battery life, etc.

[0005]

[Objects of the Invention] This invention aims at offering the rechargeable battery containing this

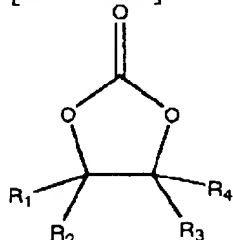
nonaqueous electrolyte while it aims at offering the nonaqueous electrolyte for rechargeable batteries which was made in view of the above-mentioned trouble, fire retardancy was highly safe, and could generate the high voltage, and was excellent in cell charge/discharge capability ability.

[0006]

[Summary of the Invention] The nonaqueous electrolyte for rechargeable batteries concerning this invention is characterized by becoming a non-aqueous solvent containing the annular carbonate expressed with the following general formula [I], and a phosphoric ester compound from an electrolyte.

[0007]

[Formula 5]



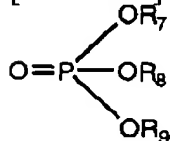
[I]

Among the formula [I], even if R1-R4 are mutually the same, you may differ. The carbon atomic number in which a hydrogen atom and a carbon atomic number include the alkyl group of 1-7 and a non-conjugated-system unsaturated bond The hydrocarbon group of 2-7, - It is CH₂OR₅ or -CH₂OCOR₆, and [the carbon atomic number in which, as for R₅ and R₆, a carbon atomic number includes an alkyl group or non-conjugated-system unsaturated bond of 1-7 showing the hydrocarbon group of 2-7], and at least 1 of R1-R4 are radicals including a non-conjugated-system unsaturated bond.

[0008] That in which the carbon atomic number which includes a non-conjugated-system unsaturated bond in at least one of the annular carbonate expressed with the above-mentioned general formula [I], and R1-R4 has the hydrocarbon group of 2-7 is desirable, and it is desirable that it is an alkenyl radical especially. moreover, among [the cyclic ester expressed with the above-mentioned general formula [I], and among R1-R4] -- at least one -CH₂OR₅ or -CH₂OCOR₆ -- it is (the carbon atomic number in which, as for R₅ and R₆, a carbon atomic number includes the alkyl group or non-conjugated-system unsaturated bond of 1-7 shows the hydrocarbon group of 2-7) -- what it has is desirable.

[0009] It is desirable that it is phosphoric ester expressed with following general formula [II] - [IV], and said phosphoric ester compound is [0010].

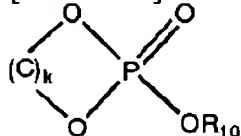
[Formula 6]



[II]

[0011]

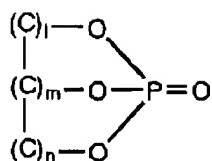
[Formula 7]



[III]

[0012]

[Formula 8]



[IV]

(Among a formula, even if R7-R10 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitute alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [you may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers. It is desirable especially that it is trimethyl phosphate. The thing of an annular carbonate and a chain-like carbonate for which said non-aqueous solvent includes 1. kind at least is still more desirable. As for an electrolyte, it is desirable that it is lithium salt.

[0013] The nonaqueous electrolyte rechargeable battery concerning this invention is characterized by a metal lithium, the lithium content alloy, the negative electrode containing either of the carbon materials in which the dope and dedoping of a lithium ion are possible, the positive electrode that contains either the multiple oxide of a lithium and transition metals, carbon materials or such mixture as positive active material, and including said nonaqueous electrolyte for rechargeable batteries as the electrolytic solution as a negative-electrode active material.

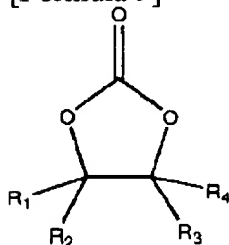
[0014]

[Detailed Description of the Invention] Hereafter, the nonaqueous electrolyte concerning this invention and the nonaqueous electrolyte rechargeable battery using this nonaqueous electrolyte are explained concretely. The nonaqueous electrolyte for rechargeable batteries concerning this invention consists of a non-aqueous solvent containing a specific annular carbonate and a specific phosphoric ester compound, and an electrolyte.

[0015] What is expressed with the following general formula [I] as an annular carbonate used by annular carbonate this invention is used.

[0016]

[Formula 9]



[I]

Among the formula [I], even if R1-R4 are mutually the same, you may differ. The carbon atomic number in which a hydrogen atom and a carbon atomic number include the alkyl group of 1-7 and a non-conjugated-system unsaturated bond The hydrocarbon group of 2-7, - It is CH₂OR₅ or -CH₂OCOR₆ (the carbon atomic number in which, as for R₅ and R₆, a carbon atomic number includes the alkyl group or non-conjugated-system unsaturated bond of 1-7 shows the hydrocarbon group of 2-7), and is the radical in which at least one of R₁-R₄ includes a non-conjugated-system unsaturated bond.

[0017] What the carbon atomic number in which at least one of R₁-R₄ includes a non-conjugated-system unsaturated bond has the hydrocarbon group of 2-7, and has -CH₂OR₅ or -CH₂OCOR₆ (the carbon atomic number in which R₅ and R₆ include a non-conjugated-system unsaturated bond shows the hydrocarbon group of 2-7) is desirable as cyclic ester expressed with such an above-mentioned general formula [I] by this invention. It is desirable that a carbon atomic number including such a non-conjugated-system unsaturated bond is an alkenyl radical as a hydrocarbon group of 2-7.

[0018] As an annular carbonate expressed with such a formula [I] 4-vinyl ethylene carbonate, 4, and 4-divinyl ethylene carbonate, Vinyl ethylene carbonate derivative; 4-vinyl-4-methyl ethylene carbonate, such as 4 and 5-divinyl ethylene carbonate, 4-vinyl-5-methyl ethylene carbonate, 4-vinyl -4, 5-dimethyl ethylene carbonate, 4-vinyl -5, 5-dimethyl ethylene carbonate, 4-vinyl - Alkylation vinyl ethylene carbonate derivative; 4-allyloxy methyl ethylene carbonate, such as 4, 5, and 5-trimethylethylene carbonate, Allyloxy methyl ethylene carbonate derivative; 4-methyl-4-allyloxy methyl ethylene carbonate, such as 4 and 5-diaryl oxymethyl ethylene carbonate, Alkylation allyloxy methyl ethylene carbonate, such as 4-methyl-5-allyloxy methyl ethylene carbonate; 4-acrylic oxymethyl ethylene carbonate, Acrylic oxymethyl ethylene carbonate derivative; 4-methyl-4-acrylic oxymethyl ethylene carbonate, such as 4 and 5-JIAKURIRU oxymethyl ethylene carbonate, Alkylation acrylic oxymethyl ethylene carbonate, such as 4-methyl-5-acrylic oxymethyl ethylene carbonate, etc. is mentioned.

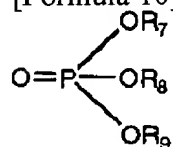
[0019] Among these, the thing containing vinyl ethylene carbonate derivatives, such as 4-vinyl ethylene carbonate, 4, and 4-divinyl ethylene carbonate, 4, and 5-divinyl ethylene carbonate, is desirable.

[0020] There is an effect of improving the fall of the charge-and-discharge effectiveness of the cell produced in case a phosphoric ester compound is added, and a load characteristic in such an annular carbonate.

As a phosphoric ester compound used by phosphoric ester compound this invention, the phosphoric ester expressed with following general formula [II] - [IV] is used preferably.

[0021]

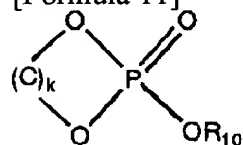
[Formula 10]



[II]

[0022]

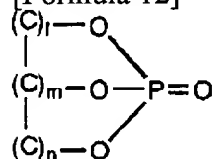
[Formula 11]



[III]

[0023]

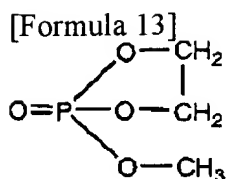
[Formula 12]



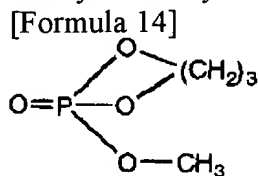
[IV]

(Among a formula, even if R7-R10 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitute alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [you may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers.

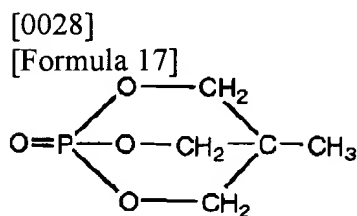
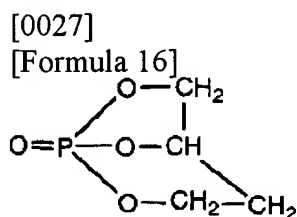
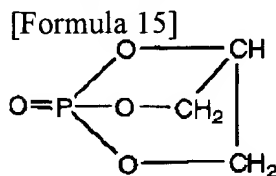
Specifically as phosphoric ester expressed with a formula [II], trimethyl phosphate, triethyl phosphate, TORIPURO pill phosphate, tributyl phosphate, dimethyl ethyl phosphate, methyl diethyl phosphate, etc. are mentioned. Specifically as phosphoric ester expressed with a formula [III], it is methyl ethylene phosphate and [0024].



Methyl trimethylene phosphate [0025]



**** is mentioned. Specifically as phosphoric ester expressed with a formula [IV], it is [0026].



Trimethylolethane phosphate etc. is mentioned.

[0029] In respect of fire-resistant grant, since the effect is large, trimethyl phosphate and phosphoric-acid triethyl are desirable, and especially trimethyl phosphate is [among these] desirable.

[0030] In the nonaqueous electrolyte for rechargeable batteries concerning non-aqueous-solvent this invention, the non-aqueous solvent containing the annular carbonate expressed with the above general formulas [I] and a phosphoric ester compound is used. As for said phosphoric-acid ESUDERU compound, in the binary system of an annular carbonate and a phosphoric ester compound, it is desirable to be preferably contained in 90 - 99.9% of the weight of the amount still more preferably 80 to 99.99% of the weight 60 to 99.999% of the weight in a non-aqueous solvent. If the phosphoric ester compound is contained in the non-aqueous solvent in such an amount, sufficient fire retardancy for the nonaqueous electrolyte for rechargeable batteries can be given.

[0031] Moreover, as for the annular carbonate expressed with a general formula [I], it is desirable to be preferably added in 0.1 - 10% of the weight of the amount still more preferably 0.01 to 20% of the weight 0.001 to 40% of the weight to a non-aqueous solvent. If the annular carbonate expressed with a general formula [I] in a non-aqueous solvent in such an amount is added, the fall of the charge-and-discharge effectiveness of the cell produced in case a phosphoric ester compound is added, and a load characteristic is fully improvable.

[0032] With the non-aqueous solvent used by this invention It is desirable to contain carbonates, such as other annular carbonates and a chain-like carbonate, in addition to the annular carbonate expressed with a general formula [I] and a phosphoric ester compound. By including such a carbonate, the charge-and-discharge effectiveness and the load characteristic of a cell are further improvable. As other annular carbonates, ethylene carbonate, propylene carbonate, butylene carbonate, etc. are mentioned. these -- one sort -- or two or more sorts may use it, mixing. The mixed solvent of ethylene carbonate, propylene carbonate or ethylene carbonate, and propylene carbonate is preferably used among these annular carbonates. If these annular carbonates are contained, it is possible to raise the solubility of the electrolyte in low temperature, transportation of an electrolyte can become easy, and the electrical conductivity of the electrolytic solution can be raised further.

[0033] As a chain-like carbonate, dimethyl carbonate, methylethyl carbonate, diethyl carbonate, methylpropyl carbonate, methyl isopropyl carbonate, ethyl propyl carbonate, etc. are mentioned. these -- one sort -- or two or more sorts may use it, mixing. Since dimethyl carbonate can raise the self-extinguishing of the electrolytic solution among these chain-like carbonates, it is desirable.

[0034] If these chain-like carbonic acid ESUDERU is contained in the non-aqueous solvent, it is possible to make low viscosity of the nonaqueous electrolyte for rechargeable batteries, and electrolytic solubility can be raised further and it can consider as the electrolytic solution excellent in the electrical conductivity in ordinary temperature or low temperature. The above chain-like carbonates and annular carbonates can also be mixed and used.

[0035] In the case of the three-component system which mixes and uses other the above cyclic ester and chain-like carbonates for the annular carbonate and phosphoric ester compound which are expressed with a general formula [I], the annular carbonate expressed with a general formula [I] is 0.001 - 40 % of the weight usually preferably used at 0.1 - 5% of the weight of a rate still more preferably 0.01 to 20% of the weight to the non-aqueous-solvent whole quantity.

[0036] case [moreover,] it is the same -- a phosphoric ester compound -- the non-aqueous-solvent whole quantity -- receiving -- usually -- it is preferably used at 3 - 60% of the weight of a rate still more preferably one to 99.99% of the weight 0.1 to 99.999% of the weight -- having -- other cyclic ester and chain-like carbonates -- the non-aqueous-solvent whole quantity -- receiving -- usually -- it is preferably used at 35 - 96.9% of the weight of a rate still more preferably 98.9 or less % of the weight 99.899 or less % of the weight.

[0037] If it is possible to raise the electrical conductivity of the nonaqueous electrolyte for rechargeable batteries if other annular carbonates are contained in the non-aqueous solvent in such an amount and the chain-like carbonate is contained, the nonaqueous electrolyte for rechargeable batteries excellent in self-extinguishing can be obtained.

[0038] The annular carbonate expressed with the above-mentioned phosphoric ester and a general formula [I] to the non-aqueous solvent used by this invention further again, The methyl formate usually used as a non-aqueous solvent for cells besides other annular carbonates and a chain-like carbonate, Ethyl formate, propyl formate, methyl acetate, ethyl acetate, propyl acetate, Chain-like ether, such as chain-like ester, such as methyl propionate and ethyl propionate, and dimethoxyethane, Amides, such as cyclic ether, such as a tetrahydrofuran, and dimethylformamide *****-BAMETO, such as methyl-N and N-dimethyl carver mate Annular sulfones, such as cyclic ester, such as gamma-butyrolactone, and a sulfolane Non-aqueous solvents, such as annular urea, such as cyclic amide [, such as annular carver mates, such as N-methyl OKISASORIJINON and N-methyl pyrrolidone,], N, and N-dimethyl imidazolidone, can be used to about 40 % of the weight to the whole quantity of a non-aqueous solvent.

[0039] As an electrolyte used by electrolyte this invention, if used as an electrolyte for nonaqueous electrolyte, it can usually be used, without being limited especially. Specifically LiPF₆, LiBF₄, LiClO₄, LiAsF₆, LiOSO₂R₁₁, LiN (SO two R₁₂) (SO two R₁₃), R₁₁-R₁₈ among LiC (SO two R₁₄) (SO two R₁₅) (SO two R₁₆) and a LiN(SO₂OR₁₇) (SO₂OR₁₈) [type You may differ, even if mutually the same, and lithium salt, such as] and LiSiF₆ which are the perfluoroalkyl radical of carbon numbers 1-6, LiC₄F₉SO₃, and LiC₃F₁₇SO₃, is used preferably. These lithium salt may be used independently, and may mix and use two or more sorts of lithium salt.

[0040] Since LiPF_6 and LiBF_4 become [fire retardancy] high by the synergism with phosphoric ester among these lithium salt, it is desirable. As for such an electrolyte, it is usually desirable to contain 0.1-3 mols /in the nonaqueous electrolyte for rechargeable batteries by the concentration of 0.5-2 mols/l. preferably 1.

The nonaqueous electrolyte rechargeable battery concerning nonaqueous electrolyte rechargeable battery this invention consists of a metal lithium, a lithium content alloy, a negative electrode containing either of the carbon materials in which the dope and dedoping of a lithium ion are possible, a positive electrode that contains either the multiple oxide of a lithium and transition metals, carbon materials or such mixture as positive active material, and aforementioned nonaqueous electrolyte for rechargeable batteries as a negative-electrode active material.

[0041] Such a nonaqueous electrolyte rechargeable battery is applicable to for example, a cylindrical nonaqueous electrolyte rechargeable battery. A cylindrical nonaqueous electrolyte rechargeable battery comes to contain the negative electrode 1 which applies a negative-electrode active material to the negative-electrode charge collector 9, and becomes it as shown in drawing 1, and the positive electrode 2 which comes to apply positive active material to the positive-electrode charge collector 10 with the cell can 5, where [of winding and a winding object] an electric insulating plate 4 is laid up and down through the SEPARATE evening 3 into which the nonaqueous electrolyte for rechargeable batteries was poured. the cell can 5 -- the cell lid 7 -- the ** ROGASU blanket 6 -- minding -- by closing, it is attached and connects with a negative electrode 1 or a positive electrode 2 electrically through negative-electrode lead 1 1 and positive-electrode lead 1 2, respectively, and it is constituted so that it may function as the negative electrode or positive electrode of a cell. In addition, a separator is a porous film.

[0042] By this cell, as for the positive-electrode lead 12, electrical installation with the cell lid 7 may be measured through the sheet metal 8 for current cutoff. By such cell, when the pressure inside a cell rises, the sheet metal 8 for current cutoff is pushed up, and deforms, positive-electrode lead 1 2 leave the above-mentioned sheet metal 8 and the welded portion, they are cut, and it is that current is intercepted as like.

[0043] As a negative-electrode active material which constitutes such a negative electrode 1, although any of doping and the carbon material which can be dedoped can be used for a metal lithium, a lithium alloy, and a lithium ion, it is [among these] desirable to use doping and the carbon material which can be dedoped for a lithium ion. Such a carbon material may be graphite, or may be amorphous carbon, and all carbon materials, such as activated carbon, a carbon fiber, carbon black, and a meso carbon micro bead, are used.

[0044] Especially in this invention, the spacing (d002) of the field (002) measured by X-ray analysis is 0.37nm or less, and if the carbon material which has a property near the graphite whose density is three or more 1.70 g/cm is desirable and uses such a carbon material, energy density of a cell can be made high. Moreover, the multiple oxide which the multiple oxide which consists of the lithium and transition metals of transition-metals oxides, such as MoS_2 , TiS_2 , MnO_2 , and V_2O_5 , and a transition-metals sulfide or LiCoO_2 and LiMnO_2 , LiMn_2O_4 , and LiNiO_2 grade is used as positive active material which constitutes a positive electrode 2, and especially consists of a lithium and transition metals is desirable.

[0045] Moreover, when a negative electrode is a lithium metal or a lithium alloy, a carbon material can also be used as a positive electrode. The mixture of a lithium, the multiple oxide of transition metals, and a carbon material can also be used as a positive electrode further again. Moreover, the nonaqueous electrolyte rechargeable battery concerning this invention is applicable also to a coin mold nonaqueous electrolyte rechargeable battery as shown in drawing 2.

[0046] disc-like in the coin mold nonaqueous electrolyte rechargeable battery of drawing 2 -- negative-electrode 1 3 -- disc-like -- positive-electrode 1 4, a separator 15, and stainless board 1 7 -- a negative electrode 13, separator 1 5, and a positive electrode 1 -- 4 and where a laminating is carried out in the stainless sequence of board 1 7, it contains to cell can 1 6 -- having -- the cell can (lid) 19 -- gasket 1 8 -- minding -- it is attached by closing. The same thing as the above is used as negative-electrode 1 3, separator 1 5, and positive-electrode 1 4. Moreover, the thing of the quality of the material of the

stainless steel which cannot corrode cell can 16 and cell can (lid) 19 easily with the electrolytic solution is used.

[0047] In addition, it may not be limited to what showed the configuration of a cell etc. to drawing 1 and drawing 2 including the nonaqueous electrolyte for rechargeable batteries which explained the nonaqueous electrolyte rechargeable battery concerning this invention above as the electrolytic solution, but you may be a square shape etc.

[0048]

[Effect of the Invention] The nonaqueous electrolyte for rechargeable batteries concerning this invention is fire retardancy, and excellent in charge/discharge capability ability, and the nonaqueous electrolyte rechargeable battery using such nonaqueous electrolyte for rechargeable batteries is safe, can generate the high voltage, and is excellent in a charge-and-discharge property.

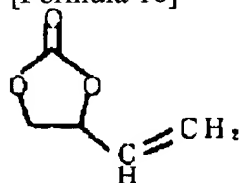
[0049]

[Example] Although an example is given and this invention is explained concretely hereafter, this invention is not limited at all by these examples.

[0050] Vinyl ethylene carbonate in the nonaqueous electrolyte for rechargeable batteries after dissolving example 1 <preparation of nonaqueous electrolyte for rechargeable batteries> LiPF₆ 15.2g (100mmol) in trimethyl phosphate (TMPA) (VEC)

[0051]

[Formula 18]



It added so that concentration might become 5% of the weight, and the nonaqueous electrolyte for rechargeable batteries was prepared (electrolytic concentration of 1.0 mols/l.).

<production of a negative electrode> -- first, it is the following, and the negative electrode 13 was made and produced.

[0052] the carbon powder 95 weight section of the mesophase pitch micro fiber Made from PETOKA (trade name: MEMBUROMMIRUDO, $d_{002}=0.336\text{nm}$, density 2.21 g/cm^3) and the polyvinylidene fluoride (PVDF) 5 weight section of a binder are mixed, and it distributes to N-methyl pyrrolidone of a solvent -- making -- a negative electrode -- a mixture -- the slurry (the shape of a paste) was prepared. this negative electrode -- a mixture -- after making the negative-electrode charge collector with a thickness of 20 micrometers made from band-like copper foil apply and dry a slurry, the band-like carbon negative electrode was obtained. such a negative electrode -- the thickness of a mixture was 25 micrometers. Furthermore, after piercing this band electrode to discoid with a diameter of 15mm, it pressed and considered as the negative-electrode electrode 13.

The <production of positive electrode> positive electrode 14 is the following, and was made and produced.

[0053] the LiCoO₂ (product name: HLC-21, mean particle diameter of 8 micrometers) particle 91 weight section by Honjo Chemical, the graphite 6 weight section of electric conduction material, and the polyvinylidene fluoride 3 weight section of a binder -- mixing -- a positive electrode -- preparing a mixture and distributing N-methyl pyrrolidone -- a positive electrode -- a mixture -- the slurry was obtained. The positive-electrode charge collector made from band-like aluminium foil with a thickness of 20 micrometers was made to apply and dry this slurry, it pressed, and the band-like positive electrode was obtained. such a positive electrode -- the thickness of a mixture was 40 micrometers. It considered as the positive-electrode electrode 14 by furthermore piercing this band electrode to discoid with a diameter of 15mm.

<production of a cell> -- as shown in drawing 2, after carrying out the laminating of the disc-like negative electrode 13 obtained by doing in this way, the disc-like positive electrode 14, and the separator

15 (micrometers [in thickness / 25], fine porosity polypropylene film with a diameter of 19mm) to the cell can 16 of 2032 sizes made from stainless steel in the sequence of a negative electrode 13, a separator 15, and a positive electrode 14, said nonaqueous electrolyte for rechargeable batteries was poured into the separator 15. Then, after containing the board 17 (the thickness of 2.4mm, diameter of 15.4mm) made from stainless steel, through the gasket 18 made from polypropylene, by closing the cell can (lid) 19, the airtightness in a cell was held and the coin mold nonaqueous electrolyte rechargeable battery with a diameter [of 20mm] and a height of 3.2mm was produced.

<Measurement of discharge capacity>, thus the produced discharge capacity of a nonaqueous electrolyte rechargeable battery were measured. In addition, in this example, the direction of current where Li^+ is doped by the negative electrode was considered as charge, and the direction of current dedoped was considered as discharge. Charge was performed by the 4.2V or 1mA constant current constant-potential charge method, and when the charging current became below 50microA, it considered as termination. Discharge was performed by 1mA constant current, and when voltage amounted to 2.7V, it considered as termination. From the charge capacity of this charge-and-discharge cycle, and discharge capacity, charge-and-discharge effectiveness was calculated by the degree type. A result is shown in a table 1.

[0054]

[Equation 1]

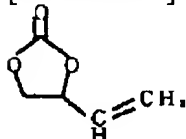
$$\text{充放電効率 (\%)} = \frac{\text{放電容量 (mAh/g)}}{\text{充電容量 (mAh/g)}} \times 100$$

[0055] The Manila paper for separators with a thickness of 0.04mm cut with a length of 30cm a 15mm and in the shape of a strip of paper in the beaker containing the nonaqueous electrolyte for the <self-extinguishing evaluation of nonaqueous electrolyte for rechargeable batteries> aforementioned rechargeable batteries was dipped 1 minute or more. The superfluous nonaqueous electrolyte for rechargeable batteries which drips from Manila paper was wiped with the beaker wall, the support needle of the sample base which has a support needle at intervals of 2.5cm was stabbed with Manila paper, and it fixed horizontally. The sample base which fixed Manila paper was put into the metal box of 25 cm x 25 cm x 50 cm, the end was lit with the writer, the length with which separator paper burned was measured, and the case where combustion length was under 1cm was estimated that there is self-extinguishing. A result is shown in a table 1.

[0056] Vinyl ethylene carbonate in the nonaqueous electrolyte for rechargeable batteries after dissolving LiPF_6 15.2g (100mmol) in the mixed solvent (mixed weight ratio EC:DMC:TMPA= 37.6:56.7:5.2) of ethylene carbonate (EC), dimethyl carbonate (DMC), and trimethyl phosphate (TMPA) like example 2 example 1 (VEC)

[0057]

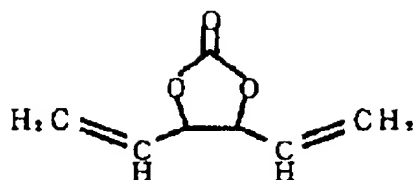
[Formula 19]



It added so that concentration might become 0.5% of the weight, and the charge-and-discharge effectiveness of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 1 except having prepared the nonaqueous electrolyte for rechargeable batteries (electrolytic concentration of 1.0 mols/l.). A result is shown in a table 1.

[0058] It sets in the example 3 example 2, and is 4 and 5-divinyl ethylene carbonate [0059] instead of vinyl ethylene carbonate.

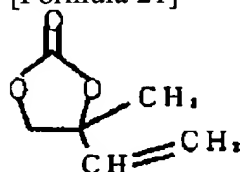
[Formula 20]



The charge-and-discharge effectiveness of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 2 except having used it. A result is shown in a table 1.

[0060] It sets in the example 4 example 2, and they are 4-methyl and 4-vinyl ethylene carbonate [0061] instead of vinyl ethylene carbonate.

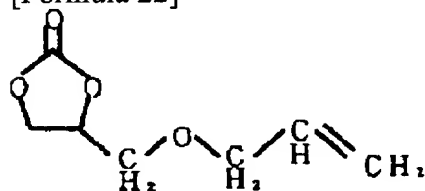
[Formula 21]



The charge-and-discharge effectiveness of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 2 except having used it. A result is shown in a table 1.

[0062] It sets in the example 5 example 2, and is allyloxy methyl ethylene carbonate [0063] instead of vinyl ethylene carbonate.

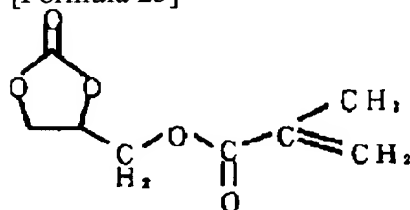
[Formula 22]



except for having used it -- an example 2 -- the same -- carrying out -- the charge-and-discharge effectiveness of a cell -- ** -- self-extinguishing evaluation of the electrolytic solution -- it carried out. A result is shown in a table 1.

[0064] It sets in the example 6 example 2, and is metacryloxy methyl ethylene carbonate [0065] instead of vinyl ethylene carbonate.

[Formula 23]



The charge-and-discharge effectiveness of a cell and the self-extinguishing of the electrolytic solution were evaluated like the example 2 except having used it. A result is shown in a table 1.

[0066]

[A table 1]

	非水溶媒組成(重量%)					初回充放 電効率(%)	自己 消火 性
	EC	DMC	TMPA	環状 カーボネート	添加量 (重量%)		
実施例1	0	0	95.0	ビニルEC	5.0	87.3	あり
実施例2	37.6	56.7	5.2	ビニルEC	0.5	95.6	あり
実施例3	37.6	56.7	5.2	シビニル EC	0.5	95.6	あり
実施例4	37.6	56.7	5.2	4-メチル,4- ビニルEC	0.5	89.8	あり
実施例5	37.6	56.7	5.2	アリルオキシメ チルEC	0.5	89.4	あり
実施例6	37.6	56.7	5.2	メタクリルオキ シメチルEC	0.5	90.5	あり

[Translation done.]

* NOTICES *

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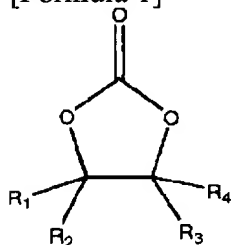
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Nonaqueous electrolyte for rechargeable batteries characterized by becoming a non-aqueous solvent containing an annular carbonate expressed with the following general formula [I], and a phosphoric ester compound from an electrolyte.

[Formula 1]



[I]

(Among the formula [I], even if R1-R4 are mutually the same, you may differ.) The carbon atomic number in which a hydrogen atom and a carbon atomic number include the alkyl group of 1-7 and a non-conjugated-system unsaturated bond The hydrocarbon group of 2-7, - it is CH₂OR₅ or -CH₂OCOR₆, and is the radical in which [the carbon atomic number in which, as for R₅ and R₆, a carbon atomic number includes an alkyl group or non-conjugated-system unsaturated bond of 1-7 showing the hydrocarbon group of 2-7], and at least 1 of R1-R4 include a non-conjugated-system unsaturated bond.

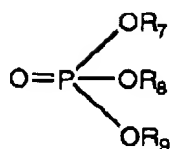
[Claim 2] Nonaqueous electrolyte for rechargeable batteries according to claim 1 characterized by a carbon atomic number to which an annular carbonate expressed with the above-mentioned general formula [I] includes a non-conjugated-system unsaturated bond in at least one of R1-R4 having a hydrocarbon group of 2-7.

[Claim 3] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to which an annular carbonate expressed with the above-mentioned general formula [I] is characterized by being what has -CH₂OR₅ or -CH₂OCOR₆ (a carbon atomic number in which R₅ and R₆ include a non-conjugated-system unsaturated bond shows a hydrocarbon group of 2-7.) in at least one of R1-R4.

[Claim 4] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to 3 to which a carbon atomic number including said non-conjugated-system unsaturated bond is characterized by a hydrocarbon group of 2-7 being an alkenyl radical.

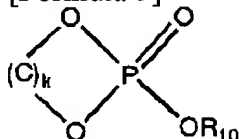
[Claim 5] Nonaqueous electrolyte for rechargeable batteries according to claim 1 characterized by said phosphoric ester compound being phosphoric ester expressed with following general formula [II] - [IV].

[Formula 2]



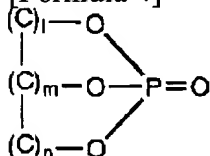
[II]

[Formula 3]



[III]

[Formula 4]



[IV]

(Among a formula, even if R7-R10 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitute alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [you may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers.

[Claim 6] Nonaqueous electrolyte for rechargeable batteries according to claim 5 to which said phosphoric ester compound is characterized by being trimethyl phosphate.

[Claim 7] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to 6 characterized by said non-aqueous solvent containing further at least one sort of carbonates chosen from annular carbonates and chain-like carbonates other than the above [I].

[Claim 8] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to 7 characterized by an electrolyte being lithium salt.

[Claim 9] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to 8 characterized by nonaqueous electrolyte for rechargeable batteries being the electrolytic solution for rechargeable lithium-ion batteries.

[Claim 10] A nonaqueous electrolyte rechargeable battery characterized by a metal lithium, lithium content alloy, negative electrode containing either of the carbon materials in which a dope and a dedope of a lithium ion are possible, positive electrode that contains either a multiple oxide of a lithium and transition metals, carbon materials or such mixture as positive active material, and having nonaqueous electrolyte for rechargeable batteries according to claim 1 to 9 as the electrolytic solution as a negative-electrode active material.

[Translation done.]